SELF-ASSEMBLED, PERFORATED MONOLAYERS FOR ENHANCED PERMSELECTIVITY IN MEMBRANES

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1. Introduction

One of the Army's primary research aims is to improve the survivability of soldiers in combat zones. One area of concern is the possibility of attack by chemical warfare agents. Current protective gear, while providing excellent protection, is heavy, bulky, and reduces the combat effectiveness of the wearer. Ideally, the next generation of protective gear will be no more cumbersome than the standard-issue Battle Dress Uniform (BDU) while maintaining its protective properties. One approach is to create a membrane that can be manufactured into a BDU, which would not allow chemical warfare agents to permeate while still allowing water (perspiration) to pass. With this goal in mind, we have been developing an ultra-thin membrane capable of blocking chemical agents, utilizing Langmuir-Blodgett (LB) films. Here, we show how ionic cross-linking of multiply-charged surfactants (a process that we have termed, "gluing") can yield LB films on the order of 6 nm thick having extraordinary barrier properties, high flux, and stability.

2. Langmuir-Blodgett Films as Permeation-Selective Membranes.

In the 1930s, Irving Langmuir and Katherine Blodgett introduced a method for fabricating monolayer and multilayer arrays of surfactants (Blodgett, 1934; Blodgett 1935; Langmuir 1934). Since that time, this Langmuir-Blodgett technique has been used, extensively, to construct a wide variety of organized thin films (Ulman, 1991). Typically, LB films are fabricated by dipping a solid support, vertically, through a surfactant monolayer at an air-water interface. For example, a single "down-trip" of a hydrophobic support from air into water results in the monolayer being transferred, such that the hydrocarbon tails are in intimate contact with the support and the polar head groups extend outward towards the bulk aqueous phase (Fig. 1). A subsequent "up-trip" generally deposits a second monolayer with a head-to-head orientation with the first deposited monolayer. Further dipping can then lead to multilayers of the surfactant (Ulman, 1991).
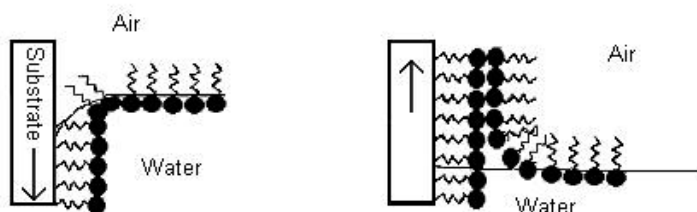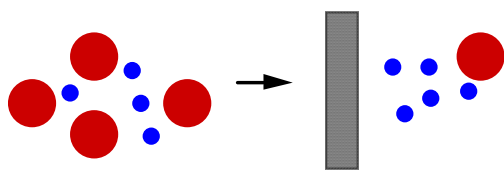

Figure 1. A stylized illustration showing a single surfactant monolayer being transferred to a hydrophobic support on a down-trip, followed by the transfer of a second monolayer on the up-trip, to form a bilayer.

The possibility of utilizing LB films as membranes for molecular separations was first recognized by Katherine Blodgett, herself. Thus, in an early patent, Blodgett noted that, "Skeleton films.... may be employed as sieves or filters for the segregation of previously non-filterable substances of molecular magnitudes" (Blodgett, 1940).

Before discussing the barrier properties of a few representative LB films, we first review some of the general principles governing membrane permeation.. An illustration of two gaseous molecules (i and j) diffusing across a hypothetical membrane is shown in Fig. 2. This figure also includes three equations that characterize gas permeation. Thus, eq 1 shows how the flux (**F**) of each permeant is related to the membrane's surface area (A), the pressure gradient (Δp) that is applied, the permeability coefficient (P) that characterizes the membrane/permeant combination, and the thickness (l) of the membrane. A normalized flux (P/l), often referred to as the permeance, is given by eq 2. Finally, the permeation selectivity (α) of the membrane, with respect to i and j, is given by the ratio of the permeances of the two gases (eq 3). The inverse relationship that exists between the flux of a gas and the thickness of the selective barrier has an important practical consequence. Specifically, thin membranes favor a high flux and high membrane productivity. The higher the permeation selectivity, the more efficient the membrane as a separating medium. Thus, two key factors

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define the utility of a membrane are the flux and the permeation selectivity. From an industrial standpoint, membrane thicknesses of ca. 100 nm are generally regarded as being very thin. The challenge of creating thinner membranes with a high flux, without introducing defects, is significant.

$$(1) \quad \textbf{Flux (cm}^3\text{/sec)} = \frac{\textbf{P} \cdot \textbf{A} \cdot \Delta \textbf{p}}{\textbf{l}}$$

$$(2) \quad \frac{\textbf{P}}{\textbf{l}} \ (\text{cm}^3\text{/cm}^2 \cdot \text{s} \cdot \text{cm Hg}) = \frac{\textbf{Flux}}{\textbf{A} \cdot \Delta \textbf{p}}$$

$$(3) \quad \alpha = \frac{\left(\frac{\textbf{P}}{\textbf{l}}\right)_i}{\left(\frac{\textbf{P}}{\textbf{l}}\right)_j}$$

Figure 2. Gaseous permeants, i (blue) and j (red) diffusing across a hypothetical membrane. Equation 1 shows the relationship between the flux, permeation coefficient (P), surface area of the membrane (A), pressure gradient used (Δp) and membrane thickness (l). Equations 2 and 3 define the normalized flux (P/l) and the permeation selectivity (α), respectively.

Because the permeation selectivity of a membrane is highly sensitive to the presence of defects, it can be a useful criterion to judge the quality of an LB film. Consider, for example, the permeation of helium and nitrogen across a hypothetical membrane. If this membrane were to contain defects, then the observed He/N_2 permeation selectivity is expected to approach the Knudsen diffusion limit—a value that is defined by Graham's law, whereby the rate of diffusion of each gas is inversely proportional to the square root of its molecular weight; that is, for He/N_2, a selectivity of 2.6 is expected. In such a case, the size of the defects is larger than the effective diameter of the permeant gases, but smaller than their mean free path. A permeation selectivity that exceeds the Knudsen diffusion limit indicates that any pores that are present are comparable in size to He and N_2.

Until recently, the permeation properties of nearly all LB films that have been investigated have been found to obey Knudsen diffusion. For example, multilayers of stearic acid that were deposited onto a silicone copolymer showed Knudsen diffusion characteristics even with films as thick as 48 layers, corresponding to a thickness of ca. 120 nm (Rose et al,, 1968; Rose et al. 1968). In one rare example in which the permeation selectivity was found to exceed the Knudsen diffusion limit, an LB film that was constructed from 40 monolayers (60 nm) of a polymeric

surfactant, **I** (X=70% and Y=30%), showed a He/N_2 selectivity of ca. 24 (Riedl et al., 2000).

stearic acid

I
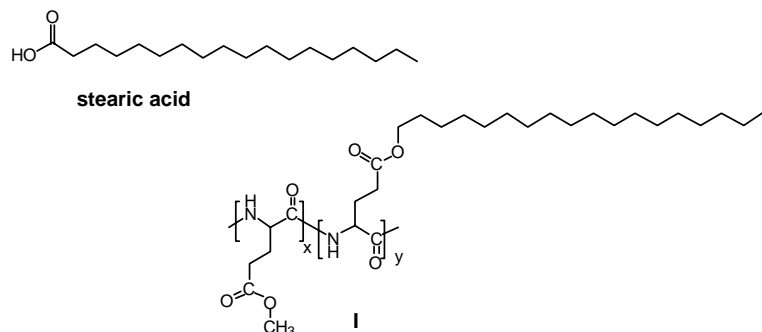
3. Perforated Langmuir-Blodgett Films.

Our own efforts in the LB film area have focused, sharply, the concept of "perforated monolayers" (Figure 3) (Hendel et al., 1997; Hendel et al., 1998; Yan et al., 2000). In brief, a monolayer of "porous" surfactants is formed at the air-water interface. Subsequent LB-deposition onto a support that is sufficiently permeable, such that gas permeation through the LB film is rate-limiting, affords the desired composite membrane. Because of their microporous structure, these perforated monolayers are expected to provide unusually high permeation selectivity due to molecular sieving.
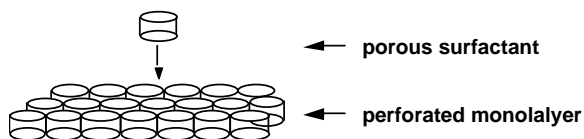

← porous surfactant

← perforated monolalyer

Figure 3. An illustration of a perforated monolayer formed from a porous surfactant.

In most of our studies, the calix[6]arene framework has been used as starting material due to its ready availability, and its ease of modification (Hendel et al., 1997; Hendel et al., 1998; Yan et al., 2000; Yan et al., 2003; Li et al., 2004). For example, in one previous report, a calix[6]arene-based surfactant (**II**) was synthesized in which amidoxime moieties were used as polar head groups and n-octyl chains served as the hydrocarbon tails (Fig. 4) (Hendel et al., 1997). The fact that the limiting area of this surfactant was nearly identical to an analog having n-hexadecyl tails provided strong support for orientation at the air-water interface; that is, where the tails of both compounds extend into air and the amidoxime groups are in intimate contact with water. Figure 5 shows a sideview and a topview of space filling models of a similar calix[6]arene having n-butyl groups as tails. In these models, the alkyl chains have been placed in an all-*anti* conformation and the calix[6]arene in a "open" conformation to give a *maximum* internal pore diameter of ca. 0.48 nm. Because

of its conformational flexibility, the effective pore diameter is likely to be smaller, approaching that of He and N_2, which are 0.16 and 0.36 nm, respectively. Single LB bilayers of **II**, which were transferred to cast films made from poly[1-(trimethylsilyl)-1-propyne] (PTMSP), were found to exhibit a He/N_2 permeation selectivity of ca. 18 (Fig. 6).
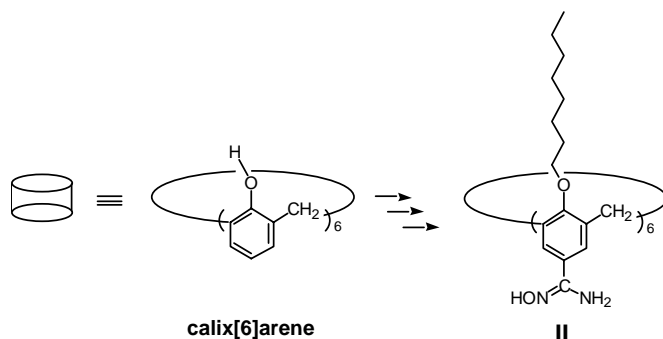

calix[6]arene   **II**

Figure 4. The calix[6]arene framework used to prepare a surfactant derivative, **II**, bearing *n*-octyl and amidoxime groups.
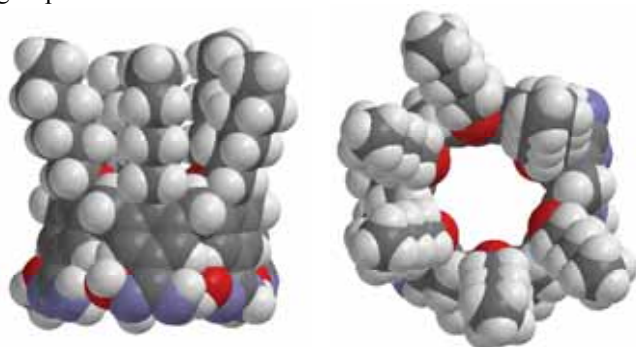

Figure 5. Space filling models of an analog of **II** having *n*-butyl "tails"; sideview (left) and topview (right).
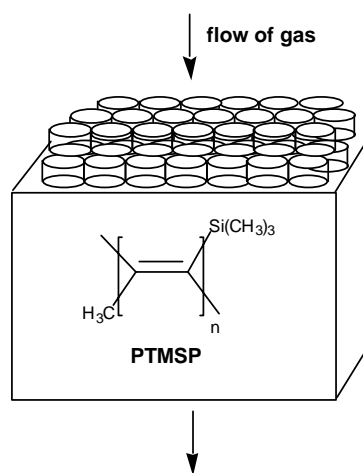

Figure 6. Composite membrane formed from a bilayer of **II** and poly[1-(trimethylsilyl)-1-propyne] (PTMSP)

Subsequent gas permeation measurements of LB bilayers of **II**, which were carried out in the

presence of water vapor, have provided strong inferential evidence for two distinct pathways for diffusion (Yan et al., 2003). Specifically, the permeability of helium (but not nitrogen) across these films was significantly reduced when the film was hydrated. These results, together with normalized fluxes that were observed for He and N_2 as a function of the pressure gradient, provided support for a model in which He (but not N_2) diffuses through individual calix[6]arenes and through gaps between calix[6]arenes. Nitrogen is presumed to diffuse only through transient gaps that develop between neighboring calix[6]arenes as a result of thermal motion.

4. Glued Langmuir-Blodgett Film.

In an effort to improve the cohesiveness of calix[6]arene-based LB film, and also their barrier properties, we synthesized ionically-cross-linkable analogs. Our presumption was that ionic cross-linking of a cationic calix[6]arene-based LB film by use of a water-soluble polyanion, would produce a two-dimensional network with enhanced stability. We further reasoned that by filling in void space (defects), the polymeric counterion would result in enhanced permeation selectivity (Fig 7). In a broader context, we were intrigued with the concept of glued LB bilayers as a new strategy for stabilizing LB films. Although there have been several reports of the use of polyions to stabilize monolayers made from singly-charged surfactants, to our knowledge, the combined use of a polyion and *multiply-charged* surfactants (required for gluing) is without precedent (Shimomura et al. 1985; Chi et al., 1991; Bruinsma et al., 1996; Panambur et al., 2004).
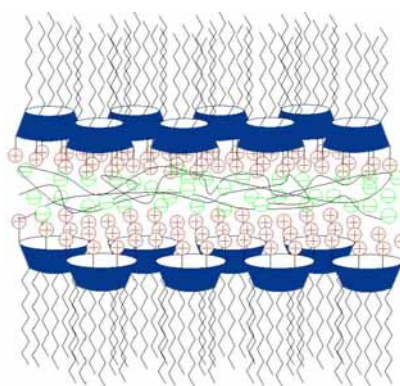

Figure 7. An illustration of a LB bilayer, made from a multiply charged calix[6]arene that has been glued together through the use of a polymeric counteron.

To demonstrate the feasibility of this concept, we used calix[6]arene **III** as a bilayer-forming amphiphile and poly(4-styrenesulfonate) (PSS) as the glue (Yan et al., 2003). Compression of **III** on the surface of pure water yielded stable monolayers having a limiting area of ca.

2.71±0.07 nm^2/molecule. Compression over an aqueous subphase containing 5.0 mM of repeat units of PSS (average M_W ca. 70,000) generated a similar surface pressure-area curve. To confirm the existence of ionic cross-linking, we measured the surface viscosity of monolayers of **III** in the absence and in the presence of PSS in the subphase. As expected, the presence of PSS dramatically increased the surface viscosity of the monolayer.

III   **PSS**   **IV**
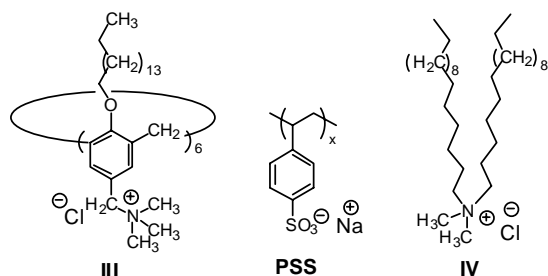
That PSS was incorporated into the LB bilayer was firmly established by a combination of X-ray photoelectron (XPS) and ellipsometric measurements. Thus, after depositing a single bilayer of **III** onto a silylated silicon wafer, subsequent analysis by ellipsometry revealed a film thickness of 5.64±0.04 nm. A similar bilayer that was prepared in the absence of PSS showed a thickness of 4.80±0.16 nm. In essence, therefore, the polyanion contributes ca. 0.84 nm to the thickness of the bilayer. Further analysis of the glued bilayer by XPS yielded insight into the location of the polyanion, its relative quantity, and the extent of ion exchange between PSS and the calix[6]arenes. By using various "take-off" angles, we were able to assess the atomic compositions at different depths. On the basis of a plot of nitrogen (N) and sulfur (S) content versus take-off angle, we were able to establish that both of these elements were buried within the LB film. In addition, the fact that the N/S atomic ratio (0.38±0.09) showed little dependency over the entire range of take-off angles, implied that both of these atoms were located at similar depths. Since no chlorine could be detected by XPS, and since the atomic percentage for Na (1.23%) plus N (1.58%) was very close to the atomic percentage of S (3.16%, 90° take-off angle), we concluded that ion exchange is essentially complete, and that the glued film contains ca. a two-fold excess of sodium 4-styrenesulfonate groups. That gluing afforded a substantial improvement in stability of the assembly was demonstrated by exposing the film to chloroform. Thus, whereas the unglued bilayer was readily removed by rinsing with chloroform, the PSS-glued analog remained fully intact, as judged by ellipsometry.

To probe the quality of glued LB bilayers of PSS and **III**, we measured their permeation selectivity with respect to He and N$_2$, using cast films of PTMSP as support material. In contrast to unglued bilayers of **III**, which exhibited a He/N$_2$ selectivity of 1.02, the glued film showed a significant decrease in the normalized flux for He, and a very dramatic decrease in the normalized flux for N$_2$; the net result being a permeation selectivity of ca. 240. Such selectivity, for an organic membrane that is less 6 nm in thickness, is without precedent. In control experiments, we found that analogous LB films that were fabricated using N,N-dimethyl-N,N-dihexadecylammonium chloride (**IV**) in place **III** showed negligible surface viscosity and negligible He/N$_2$ permeation selectivity. It should be noted that a combination of a *singly*-charged surfactant and a multiply-charged counterion (i.e., **IV** + PSS) is not capable of producing a cross-linked network. Finally, in preliminary studies, we have found that the use of certain other polyanions can produce analogous bilayers with even higher permeation selectivities. For example, replacement of PSS with poly(acrylic acid) has yielded a bilayer having a He/N$_2$ permeation selectivity of ca. 1000. Such selectivity is remarkable for a membrane that is less than 6 nm in thickness.

5. Prospectus

In principle, this technology should be applicable to one of the Army's primary goals in the area of chemical protection. Specifically, the surface modification of poly(dimethylsiloxane) by a tightly packed, and polymerized monolayer of calix[6]arenes or other surfactants could constitute an attractive semipermeable barrier, which allows the passage of water vapor (needed for evaporated cooling from the skin), but not the passage of a variety of chemical warfare agents such as nerve agents [Soman (GD), Sarin (GB), Tabun (GA), CMPF (GF), VX and VE] as well as blistering agents [Mustard (HD), Nitrogen Mustards (HN-1, HN-2, HN-3), Phosgene Oxime etc.]. Due to its ultrathin and microporous structure, one would also expect that the flux of water across such a membrane would be maximized. Thus, some of the composite membranes to be synthesized could lead to protective coatings that could be included in the fabrication of clothing that protect soldiers against exposure to chemical warfare agents.

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